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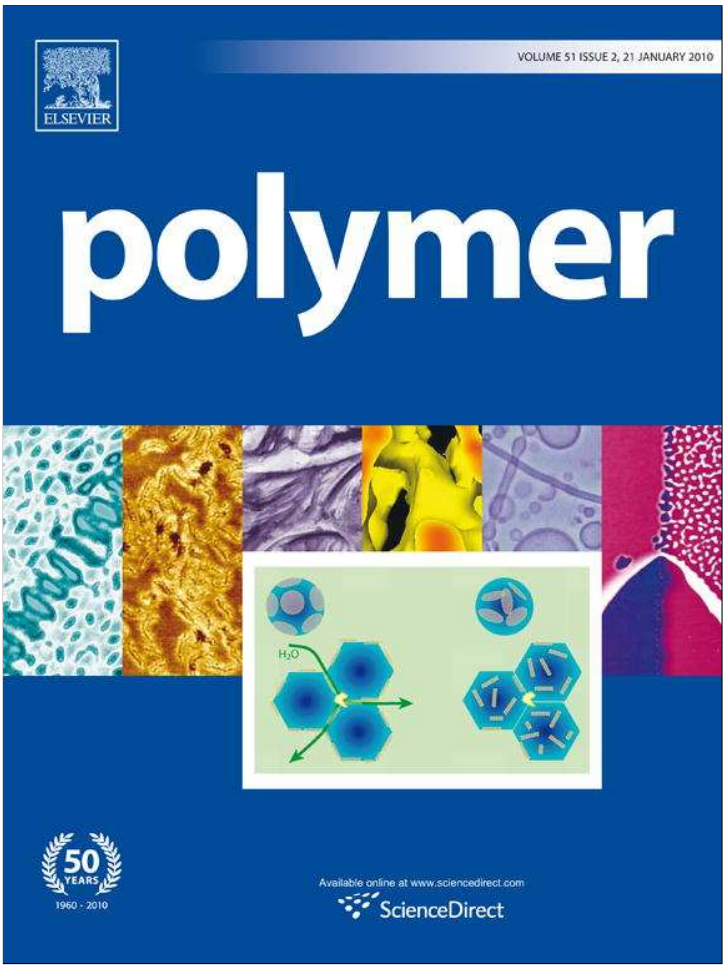

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Enhanced thermo-oxidative stability of sulfophenylated poly(ether sulfone)s

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ABSTRACT

Monophenylated poly(ether sulfone)s (Ph-PES) and diphenylated poly(ether sulfone)s (DiPh-PES), were synthesized as starting materials for the preparation of sulfonated polymers with well-defined chemical structure. Mild post-polymerization sulfonation conditions led to sulfonated Ph-PES (Ph-SPES) bearing acid groups on both the pendant phenyl group and the backbone, and sulfonated DiPh-PES (DiPh-SPES) bearing acid groups only on the two pendant phenyl groups. Both series of polymers had excellent mechanical properties, high glass transition temperatures, good thermal and oxidative stability, as well as good dimensional stability. It is interesting to note that exclusively pendant-phenyl-sulfonated (bis-sulfophenylated) DiPh-SPES copolymers possessed obviously better thermal and oxidative stability compared with the corresponding pendant-phenyl-sulfonated/main-chain-sulfonated Ph-SPES copolymers. The methanol permeability values of the membranes were in the range of 7.0×10^{-7}–9.4×10^{-8} cm^2/s at 30 °C, which is several times lower than that of Nafion 117. DiPh-SPES-50 and Ph-SPES-40 also exhibited high proton conductivity (approximately 0.13 S/cm at 100 °C).

1. Introduction

Fuel cells are electrochemical devices for transforming chemical energy directly into electricity with high efficiency, and are one of the promising clean future power sources. Extensive efforts are being made to develop proton exchange membranes (PEM)s for use in proton exchange membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC) systems[1,2]. One challenge is to find high-performance PEMs alternative to Nafion®, which is a commercial perfluorinated sulfonic acid copolymer used as the polymeric electrolyte in PEMFC systems. Sulfonated hydrocarbon-based PEMs are being widely investigated in an attempt to overcome the difficulties derived from high cost, limited operation temperature (≤80 °C), high methanol crossover, and environmental recycling uncertainties of the present commercial perfluorinated membranes [3,4].

The outstanding thermal and chemical stability of poly(arylene ether)s, and their sulfonated derivatives such as polyether sulfone (SPES) [5,6], polyetherketone (SPEK) [7,8], polyarylether (SPAE) [9,10] and polyethernitrile (SPEN) [11] are the basis for investigation as potential PEMs. Although a great variety of structures has been made, there are still challenges to be met, such as complete property evaluation of PEMs, optimization and simplification of sulfonation reactions, controllability of DS (degree of sulfonation) and the site of sulfonation, and performance enhancement and microstructure improvement of PEMs by designing polymer chemical structures [12,13].

Most of polyarylether-type PEMs are based on post-sulfonation of existing polymers or on copolymers produced from sulfonated monomers [3]. The post-polymerization sulfonation approach is well known as a relatively simple reaction procedure and one that does not necessarily result in chain degradation when sulfonation conditions are appropriate. However, difficulties may exist in the precise control of the site of sulfonation and the DS [14]. On the other hand, PEM materials prepared by copolymerization of sulfonated and non-sulfonated monomers provides random or block copolymers with the potential for better control of sulfonic acid content (SC) and defined polymer structures [15]. However, a limited number of sulfonated monomers is available and the preparation of new sulfonated monomers is not trivial. The present work addresses these issues by using a strategy of simple and mild post-sulfonation on precursor polymers having sites especially amenable to sulfonation; hence, the site of sulfonation and DS is controlled in a similar way to polymers prepared by the direct copolymerization method.

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Miyatake and Hay et al. recently reported several sulfonated polymers obtained by regioselective sulfonation with $ClSO_3H$. [16] It was suggested that polymers with the sulfonic groups attached to pendant side groups are more stable to heat, hydrolysis and oxidation. Jannasch et al. reported several SPES polymers obtained by a grafting method based on the lithiation reaction [17]. However, there are still no incontrovertible data showing that pendant-phenyl-sulfonated polymers possess better thermal and oxidative stability than their main-chain-sulfonated analogues. In addition, few pendant-phenyl-sulfonated PES polymers were synthesized by the post-sulfonation approach under mild reaction conditions [18].

Most recently, we reported that poly(aryl ether ketone)s bearing one pendant phenyl could be readily sulfonated with H_2SO_4 within several hours to form 4-phenylsulfonic acid substituted polymers. The pendant phenyl ring is highly activated towards sulfonation at the 4-position, and substitution occurs rapidly. However, it was noted that the main-chain benzene ring could be sulfonated much more slowly at the site para- to the pendant substituent when the reaction time was prolonged, to yield pendant-phenyl-sulfonated/main-chain-sulfonated polymers. [7] In order to prepare exclusively pendant-phenyl-sulfonated polymers having well-defined chemical structure and good performance, new polymeric precursors having an improved design were developed, as shown in Scheme 1. By blocking the weakly active site for sulfonation on the main chain and replacing it with an additional pendant phenyl substituent having a strongly active site for sulfonation, it is possible to prepare well-defined fully disulfonated polymers within a short reaction time.

In the present study, PES copolymers consisting of two types of segments for the control of DS and ion exchange capacity (IEC) were synthesized: one part of the segments containing pendant phenyl that are readily sulfonated (Scheme 1), and the other part of the segments that do not contain activated sites. With the aim of preparing PEM materials with well-defined structure by site-specific mild post-polymerization sulfonation, phenylated and diphenylated SPES polymers were investigated and compared. The target pendant-phenyl-sulfonated (bis-sulfophenylated) polymers were successfully prepared, and the properties relevant to PEM materials for FC applications were also evaluated.

2. Experimental

2.1. Chemicals and materials

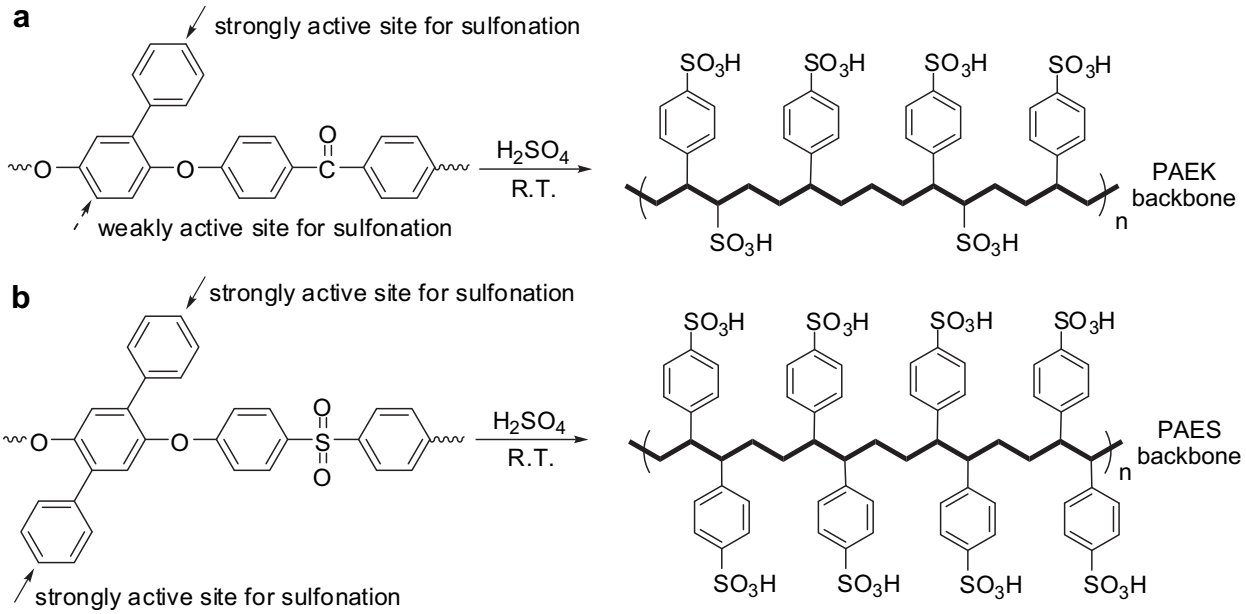
4,4′-Sulfonyldiphenol (98%) and phenylhydroquinone (97%) were obtained from Sigma–Aldrich Ltd., and recrystallized from acetone/water and toluene, respectively. Sulfuric acid (reagent grade, 95–98%) was obtained from Sigma–Aldrich Ltd. 4-Fluorophenylsulfone (99%, Sigma–Aldrich Ltd.), 2,5-diphenylquinone (96%, Alfa Aesar) and all the other chemicals were obtained from commercial sources, and used without further purification.

2.2. Synthesis of 2,5-diphenylhydroquinone

Zinc powder (0.4 mol), 2,5-diphenylquinone (0.01 mol) and water (200 mL) were placed into a 1 L three-necked flask equipped with a magnetic stirrer, a dropping funnel and a condenser. Hydrochloric acid (34 mL) was added dropwise gradually into the stirred mixture at reflux over a 6 h period. The reaction system was allowed to reflux for another 4 h at reflux. The zinc powder was removed by filtration when hot. The oil layer in the filtrate was washed with cold water several times until a solid appeared and then dried in a vacuum oven. Yellowish crystals were obtained after recrystallisation from the toluene. Yield: 85%, m.p. 226 °C (DSC). Elem. Anal. Calcd. for $C_{18}H_{14}O_2$ (262.30 g/mol): C, 82.42%; H, 5.38%. Found: C, 82.31%; H, 5.42%.

^{1}H NMR (DMSO-d_6) δ in ppm: 8.95, s, 2H, –OH; 7.57, d (8.4 Hz), 4H, H5; 7.41, t (8.4 Hz), 4H, H6; 7.29, t (8.4 Hz), 2H, H7; 6.87, s, 2H, H2.

^{13}C NMR (DMSO-d_6) δ in ppm: 146.95 (C1), 138.33 (C3), 128.84 (C6), 127.91 (C5), 127.31 (C4), 126.47 (C7), 117.39 (C2).



Scheme 1. Representations of sulfonation reactions based on: a) Mono-phenylated PAEKs in previous study (ref. 7); b) Diphenylated PES in this study.

2.3. Synthesis of starting polymers

As an example of the general synthetic procedure for polymerization, the synthesis of the copolymer DiPh-PES-50 is as follows. 2,5-Diphenylhydroquinone (2.623 g, 0.01 mol), 4,4′-sulfonyldiphenol (2.502 g, 0.01 mol), 4-fluorophenylsulfone (5.085 g, 0.02 mol), anhydrous K_2CO_3 (1.794 g, 0.013 mol), DMAc (40 mL) and toluene (20 mL) were added into a 100 mL three-necked flask equipped with a magnetic stirrer, a nitrogen inlet, and a Dean–Stark trap with a condenser. The system was allowed to reflux at about 150 °C for 4 h, and then the toluene was removed. The reaction mixture was heated to 180 °C. After 12 h, the polymerization was complete and then the resulting viscous polymer solution was precipitated into 250 mL of ethanol. The isolated polymer was refluxed in deionized water and ethanol several times to remove the salts and solvents, and dried at 120 °C for 24 h. The white DiPh-PES-50 copolymer fiber was obtained. The suffix 50 refers to the molar percentage of diphenylated polymer repeat units.

All the other starting DiPh-PES and Ph-PES polymers were prepared using the same technique.

DiPh-PES-50: ^{1}H NMR ($CDCl_3$) δ in ppm: 7.96–7.68, m, 12H; 7.45–7.15, m, 12H; 7.12–6.90, m, 12H.
DiPh-PES-100: insoluble in common deuterated solvents.
Ph-PES-50: ^{1}H NMR ($CDCl_3$) δ in ppm: 7.95–7.62, m, 12H; 7.39–6.79, m, 20H.
Ph-PES-100: ^{1}H NMR ($CDCl_3$) δ in ppm: 7.93–7.65, m, 4H; 7.35, d (8 Hz), 2H; 7.27–7.16, m, 3H; 7.13, d (3 Hz), 1H; 7.09–7.02, m, 3H; 6.99, dd (8 Hz, 3 Hz), 1H; 6.91–6.80, m, 2H. ^{13}C NMR ($CDCl_3$) δ in ppm: 161.83–161.54, m; 152.32, s; 148.33, s; 136.55, s; 135.96, s; 136.06 and 135.17, m; 129.95–129.60, m; 128.77, s; 128.37, s; 128.03, s; 123.20, s; 122.90, s; 120.49, s; 117.83 and 117.04, s.

2.4. Preparation of sulfonated polymers and their membranes

DiPh-PEK-50 (5 g) and concentrated sulfuric acid (100 mL) were added into a 250 mL flask. After stirring at room temperature for 1 week, the resulting homogeneous viscous solution was poured into a mixture of water and ice to get a silk-like solid. The solid was thoroughly washed with water until the washing water had a neutral pH. The sulfonated DiPh-PES-50 (DiPh-SPES-50) was dried in a vacuum oven at 100 °C for 24 h.

An amount of 0.5 g of the above dried polymer, DiPh-SPES-50, was dissolved in 12 mL of DMAc and the solution was filtered through a filter paper. The filtered solution was poured onto a glass plate and dried in an oven at 50 °C under a constant slow purge of nitrogen for one week. The resulting flexible membrane was dried in a vacuum oven at 120 °C for 24 h. The thickness of all membrane films was in the range of 80–120 μm.

All the other sulfonated polymers were prepared using the same procedure, and ^{1}H NMR spectroscopy was used to confirm their structure.

DiPh-SPES-50: ^{1}H NMR (DMSO-d_6) δ in ppm: 8.05–7.70, m, 12H; 7.62–7.35, m, 10H; 7.35–7.08, m, 12H.
DiPh-SPES-100: ^{1}H NMR (DMSO-d_6) δ in ppm: 7.75, d (8 Hz), 4H; 7.57, d (8 Hz), 4H; 7.46, d (8 Hz), 4H; 7.35, s, 2H; 7.11, d (8 Hz), 4H. ^{13}C NMR (DMSO-d_6) δ in ppm: 161.58, s; 148.45, s; 146.75, s; 136.27, s; 134.97, s; 134.62, s; 130.03, s; 128.73, s; 125.88, s; 124.58, s; 117.45, s.
Ph-SPES-50: ^{1}H NMR (DMSO-d_6) δ in ppm: 8.05–7.80, m, 12H; 7.62–7.36, m, 5H; 7.36–7.02 m, 13H.
Ph-SPES-100: ^{1}H NMR (DMSO-d_6) δ in ppm: 7.88–7.75, m, 4H; 7.56, d (8 Hz), 2H; 7.49–7.37, m, 3H; 7.21, m, 1H; 7.13–7.02, m, 4H. ^{13}C NMR (DMSO-d_6) δ in ppm: 163.04 and 161.93, m; 148.56, s; 148.31, s; 146.60, s; 140.57, s; 137.00, s; 136.80, s; 136.14–134.99, m; 130.71 and 130.26, s; 129.56, s; 126.44, s; 125.79, s; 122.37, s; 118.60, s.

2.5. Characterization and instruments

^{1}H, ^{13}C and 2D NMR spectra were obtained on a Varian Unity Inova NMR spectrometer operating at frequencies of 399.95 MHz for ^{1}H and 100.575 MHz for ^{13}C. Deuterated dimethylsulfoxide (DMSO-d_6) and deuterated chloroform ($CDCl_3$) were selected as the solvents.

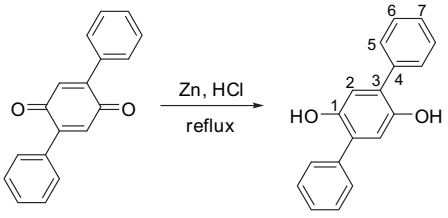
Thermal stability of the polymers was evaluated using a TA Instruments thermogravimetric analyzer (TGA) instrument model 2950. Polymer samples for TGA analysis were preheated at 150 °C for 30 min to remove moisture, and then heated at 10 °C/min from 50 °C to 800 °C under air atmosphere. The obtained TGA curves were adjusted such that the weight values of onset points were chosen as 100%. A TA Instruments differential scanning calorimeter (DSC) model 2920 was used for measuring glass transition temperature (T_g). Samples for DSC analysis were initially heated at a rate of 20 °C/min to a temperature of 10 °C below their decomposition temperature, followed by quenching them to room temperature. The samples were then heated at a rate of 10 °C/min under nitrogen atmosphere to evaluate T_g.

The proton conductivities of the membranes were calculated from AC impedance spectroscopy data, obtained over a frequency range of 1–10^7 Hz with oscillating voltage of 100 mV, using a Solartron 1260 gain phase analyzer. Specimens in the form of 20 × 10 mm strips were soaked in deionized water at room temperature for 48 h prior to the test. Specimens were clamped in a frame between two platinum electrodes, and then placed in a temperature controlled cell open to the air by a pinhole, which was equilibrated at 100% RH at ambient pressure. Measurements were carried out in four-point mode. The conductivity (σ) of the samples in the longitudinal direction was calculated, using the relationship $\sigma = L/(R \times d \times W)$ where L is the distance between the electrodes, d and W are the thickness and width of the sample stripe respectively. R was derived from the low intersect of the high frequency semi-circle on a complex impedance plane with the Re (Z) axis.

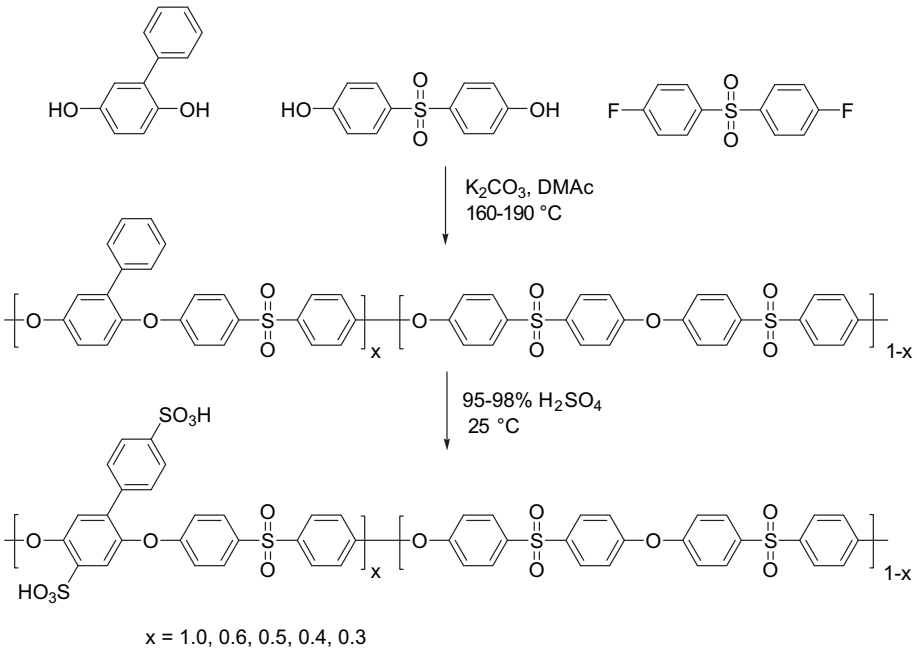
Mechanical properties of the thin films were evaluated at room temperature on an Instron 5565 instrument at a strain rate of 10 mm/min, and a 500 N load cell was used. The samples were immersed in water for 48 h, and cut into a dumbbell shape (DIN-53504-S3A).

2.6. Inherent viscosities, water uptake and swelling ratio measurements

Inherent viscosities (η_{inh}) were measured using an Ubbelohde viscometer at a polymer concentration of 0.5 g/dL in DMAc solutions at 30 °C.



Scheme 2. Synthesis of 3,5-diphenylhydroquinone.



Scheme 3. Synthesis of poly(ether sulfone)s bearing acid groups on both the main-chain and pendant-phenyl substituent.

Before testing the water uptake and swelling ratio of the samples, the membranes were dried at 100 °C overnight prior to the measurements. After measuring the lengths and weights of dry membranes, the sample films were soaked in deionized water for 24 h at predetermined temperatures. Before measuring the lengths and weights of hydrated membranes, the water was removed from the membrane surface by blotting with a paper towel.

The water uptake content was calculated by:

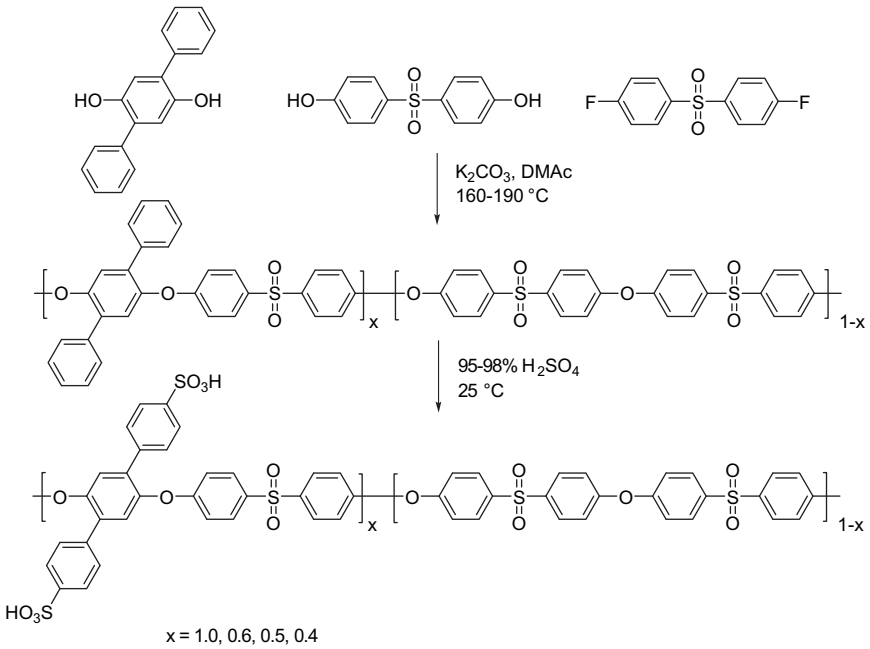
$$\text{Water uptake (wt.\%)} = \frac{\omega_{wet} - \omega_{dry}}{\omega_{dry}} \times 100\%.$$

Where ω_{dry} and ω_{wet} are the weights of dried and wet samples respectively.

The swelling ratio was calculated by:

$$\text{Swelling ratio}(\%) = \frac{l_{wet} - l_{dry}}{l_{dry}} \times 100\%.$$

Where l_{dry} and l_{wet} are the lengths of dry and wet samples respectively.



Scheme 4. Synthesis of poly(ether sulfone)s bearing acid groups on pendant-phenyl substituents.

2.7. Oxidative stability, ion exchange capacity (IEC), and methanol permeability

Oxidative stability of the membranes was tested by immersing the films into Fenton's reagent (3% H_2O_2 containing 2 ppm $FeSO_4$) at 80 °C. The dissolution time (t) of polymer membranes into the reagent was used to evaluate oxidative resistance. IEC of the sulfonated polymers was measured using a typical titration method. The films in acid form were equilibrated with excess 1 M NaCl for 24 h. The amount of the H^+ released from the membranes was determined by titration of 0.1 M NaOH aqueous solution and phenolphthalein as an indicator. The IEC was calculated according to the equation: [IEC (meq g^{-1}) = ($V_{NaOH} \times C_{NaOH}$)/Ws], where Ws is the dry weight (mg) of the sample and V_{NaOH} and C_{NaOH} are the volume (mL) and molar concentration of NaOH solution, respectively.

Methanol permeability was measured using a simple two-compartment glass diffusion cell. A membrane (2 cm × 2 cm) was placed between two silicone rubber gaskets and with the two compartments clamped together around the gaskets. The active area of the membrane was 1.757 cm^2. Compartment A was filled with 100 mL of 10% v/v (2.47 M) methanol with an internal standard of 0.2% v/v (0.022 M) 1-butanol in aqueous solution. Compartment B was filled with 100 mL of 0.2% v/v 1-butanol solution. The diffusion cell was placed in a water bath held at 30 °C and each compartment was stirred by a separate stir plate to ensure uniform stirring. Samples (4 μL each) were removed from compartment B at intervals of approximately 15 min each. Methanol concentrations were determined by ^{1}H NMR spectroscopy. The method to calculate the methanol permeability is reported in a previous study [19].

3. Results and discussion

Sulfonation is an electrophilic reaction, and the reaction rate and site of substitution are influenced by the position and type of substituents on the benzene rings. Although the sulfonation conditions for polymers are often more vigorous than those used for simple low-MW compounds, several series of polymers have been be sulfonated under mild sulfonation conditions [20,21]. The monophenylated polymers [7] wherein sulfonated sites occur both on the side chain and main chain may be less desirable in terms of PEM properties such as chemical stability and ability to go some degree of phase separation between hydrophilic and hydrophobic regions. In

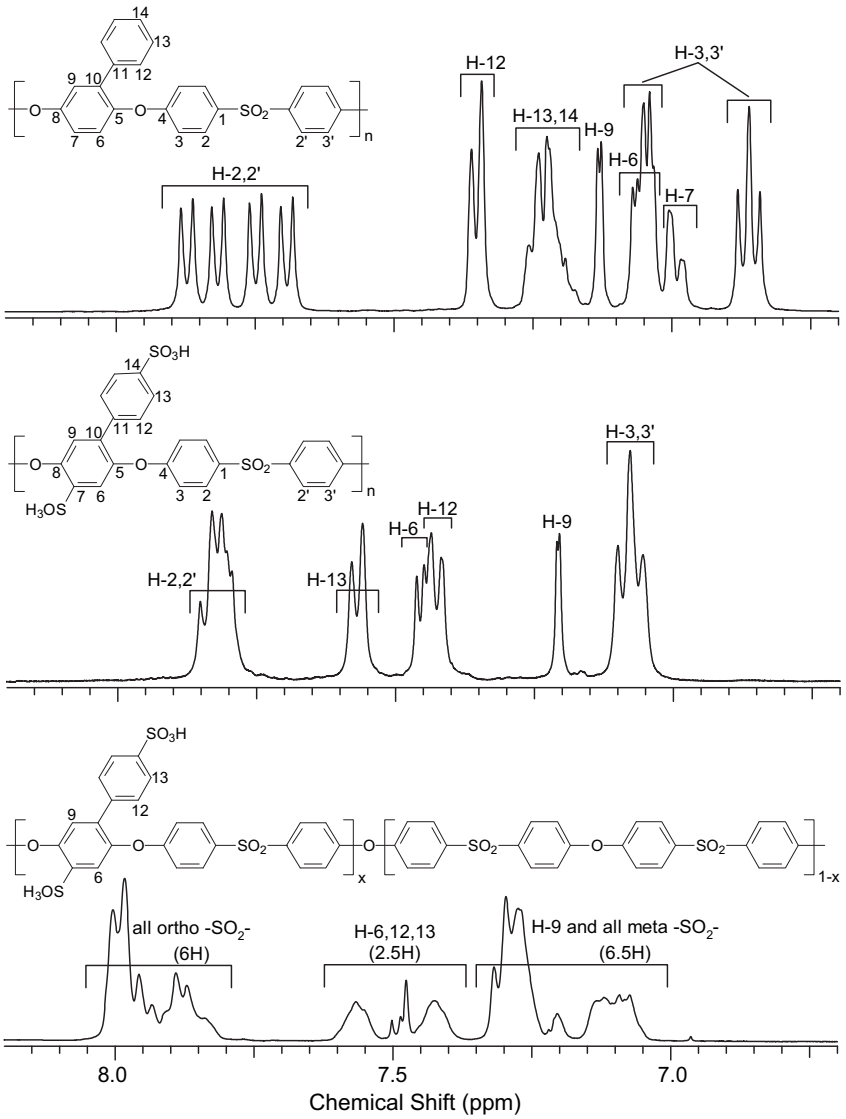


Fig. 1. From top to bottom, ^{1}H NMR spectra of Ph-PES-100 ($CDCl_3$), Ph-SPES-100 (DMSO-d_6) and Ph-SPES-50 ($x = 0.5$) (DMSO-d_6).

order to provide exclusively pendant-phenyl-sulfonated poly(arylene ether)s via post-polymerization sulfonation of phenylated polymers, a series of diphenylated aromatic poly(ether sulfone)s was prepared. The starting poly(ether sulfone) copolymers were based on a diphenylated bisphenol monomer (Scheme 2), composed of sulfonatable segments (activated by diphenylated moieties) and non-sulfonatable segments (deactivated by the sulfone linkage). For comparative purposes, mono-phenylated poly(ether sulfone) analogues were prepared to study the sulfonation reaction and properties of the resulting copolymers.

In order to obtain PEM materials with well-defined properties by the post-polymerization sulfonation approach, it is necessary to prepare polymers with specific sites that are strongly activated to sulfonation and preferably ones that require only mild sulfonation conditions to circumvent any chain degradation. In the present study, it is notable that the sulfonation reaction rate was faster than that of Victrex PEEK. Under the same reaction conditions, about one month was required to achieve fully sulfonated PEEK (DS ~ 1) [22]. Both the mono-phenylated and diphenylated PAES polymers showed good controllability of reaction sites. For the mono-phenylated SPAES series, one acid substituent was found at the 4-position of the pendant-phenyl groups, and another acid substituent occurred on the main-chain. NMR spectra and titration tests for IEC showed DS values of 2.0 under these reaction conditions. Different from the mono-phenylated PAES polymers, which led to pendant-phenyl-sulfonated/main-chain-sulfonated polymers, the sulfonation of diphenylated polymers led exclusively to pendant-phenyl-sulfonated polymers (Schemes 3 and 4), as confirmed by NMR.

Figs. 1 and 2 show the aromatic region for the ^{1}H NMR spectra of unsulfonated and sulfonated polymers. The assignment of every proton frequency was carried out with the help of various 1D and 2D homo-nuclear (^{1}H–^{1}H) and hetero-nuclear (^{1}H–^{13}C) NMR experiments. The information obtained from the peak intensities was also very helpful in the characterization of the more complex copolymer spectra. It was first necessary to understand where the sulfonation had occurred on the polymer backbone. The determination of the sulfonation sites was done using the information supplied by the peak integration values from the ^{1}H NMR and by the 2D pulse sequences. NMR of the sulfonated homopolymers confirmed what is normally expected from this electrophilic aromatic substitution reaction: the sulfonation occurred at the para

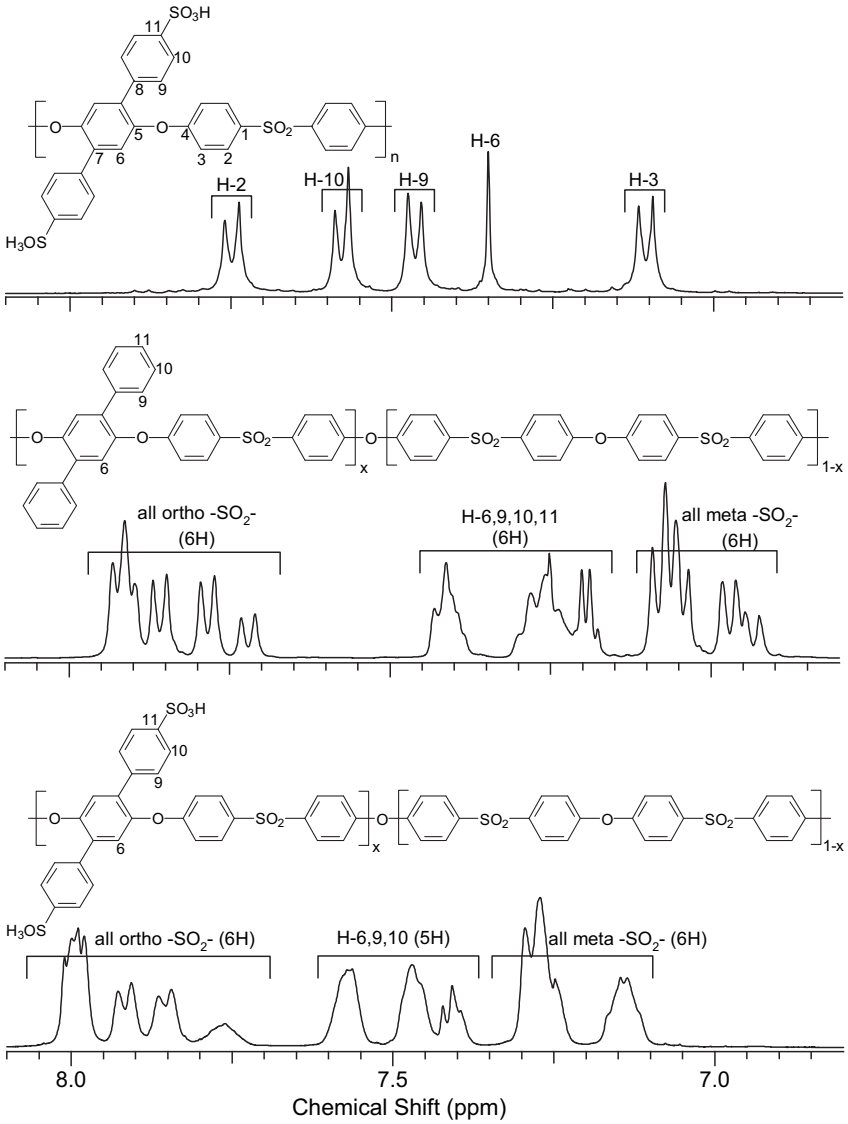


Fig. 2. From top to bottom, ^{1}H NMR spectra of Di-Ph-SPES-100 (DMSO-d_6), Di-Ph-PES-50 ($CDCl_3$) and Di-Ph-SPES-50 ($x = 0.5$) (DMSO-d_6).

position of the pendant phenyl group for both Ph-SPES and DiPh-SPES polymers and it also occurred at the ortho-oxygen sites of the Ph-PES polymers as illustrated in Fig. 1. A 2D ROESY spectrum was required to unambiguously distinguish H-6 from H-9 in the Ph-SPES-100 polymer. H-9 showed coupling through space with H-12 while H-6 showed coupling with H-3. The lack of symmetry and random distribution on position 9 or 10 of the pendant phenyl groups in the repeat units of the Ph-(S)PES polymers explains the presence of multiple peaks in both ^{1}H and ^{13}C NMR. For example, H-2,2′ and H-3,3′ of Ph-PES-100 and Ph-SPES-100 appear at different frequencies depending on whether they are spatially located near the phenyl group (phenyl at the 10 position as illustrated in Fig. 1) or away from them (phenyl at the 9 position). This is particularly apparent in the Ph-PES-100 spectrum of Fig. 1. Strong hydrogen bonding between the $-SO_3H$ of Ph-SPES is possibly also causing H-6 and H-9 to appear as multiple peaks due to different conformation of the polymer in DMSO-d_6. Those peaks appear to be spin-coupled doublets, although in fact they are non-coupled multiplets. On the other hand, the symmetry and the distance from the polymer main chain of the $-SO_3H$ groups in DiPh-SPES-100 resulted in a series of single peaks for every proton as illustrated by the simple ^{1}H NMR pattern in Fig. 2. In addition to the peak

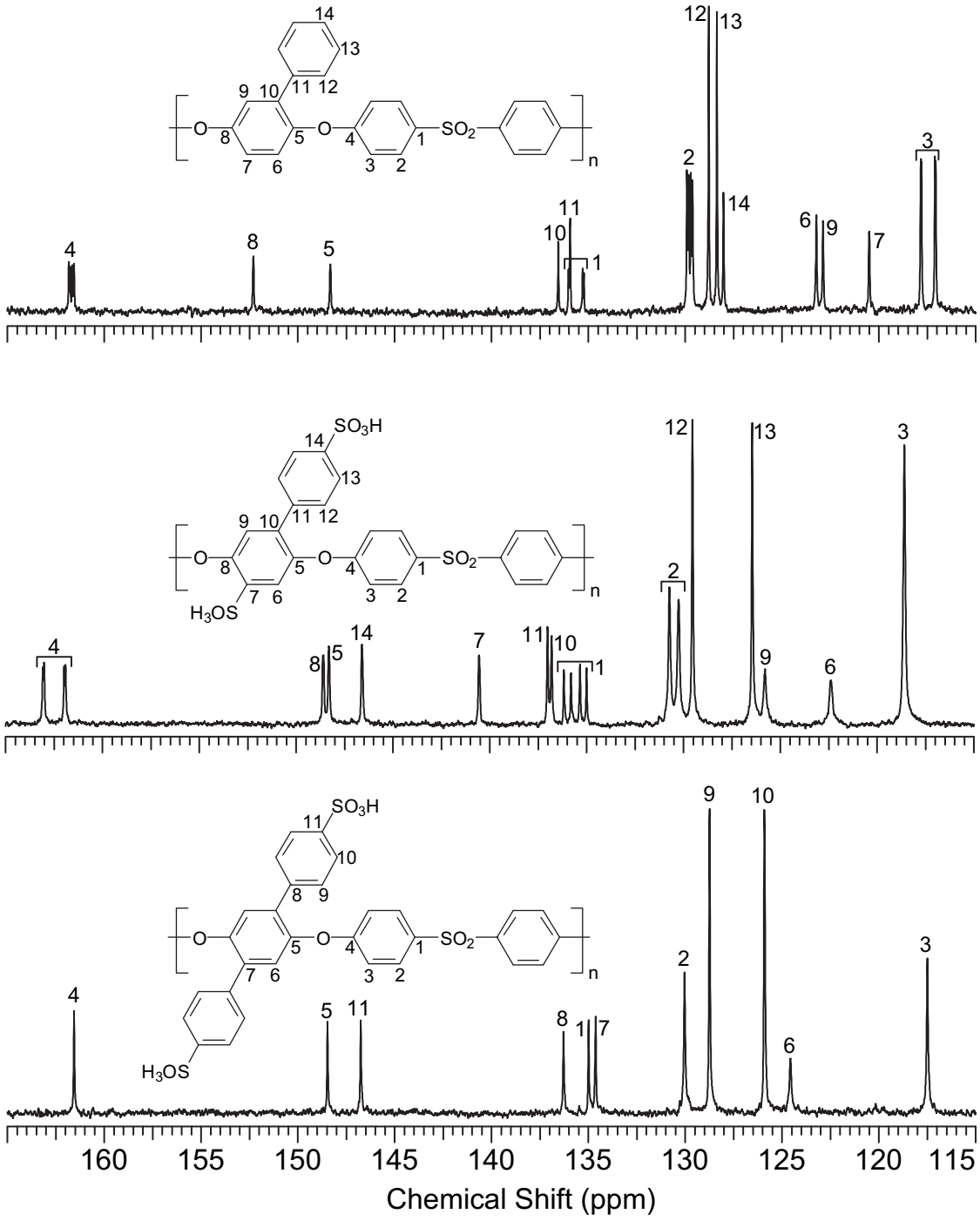


Fig. 3. From top to bottom, ^{13}C NMR spectra of Ph-PES-100 ($CDCl_3$), Ph-SPES-100 (DMSO-d_6) and DiPh-SPES-100 (DMSO-d_6).

assignments, the peak intensities also confirmed the di-substitution of the Ph-SPES and DiPh-SPES homopolymers. Fig. 1 also shows the copolymer Ph-SPES-50 and the integration values for selected areas. Knowing which proton signal is present in each area makes the verification of the copolymer ratios a simple task. For example, the spectrum of Ph-SPES-50 in Fig. 1 shows an experimental proton ratio of 6H:2.5H:6.5H which is expected from the structure displayed above the spectrum where $x = 0.5$. Similarly, Fig. 2 shows the spectra of DiPh-SPES-50 before and after sulfonation. Once again, the integration values of selected areas helped in assessing the copolymer ratio (x:1–x) and the DS on the pendant phenyl groups. Finally, Fig. 3 shows the ^{13}C NMR spectra of unsulfonated Ph-PES-100 and sulfonated Ph-SPES-100 and DiPh-SPES-100; DiPh-PES-100 is not shown due to its poor solubility properties in the NMR solvents. As seen before in ^{1}H NMR, symmetry in the DiPh-SPES-100 results in fewer peaks compared with the Ph-(S)PES polymers.

Ion exchange capacity (IEC) is another important method to evaluate the degree of sulfonation reaction, which is highly relevant with the exchangeable ions of polymer membranes. The IEC data from titration test were in the range of 1.91–1.13 meq/g, which were close to the expected values. The DS was readily controlled by adjusting the monomer feed ratios in the copolymers. This synthetic strategy has a considerable advantage over the normal method of controlling DS by reaction time and temperature [23].

Glass transition temperature (T_g) is an important parameter for applications of amorphous polymers. High T_gs are usually required for PEM materials to operate at higher temperature [24]. For all the samples, only one transition temperature was observed in the DSC curve before the decomposition temperature, which indicated their amorphous nature. As listed in Table 1, the non-sulfonated starting polymers had high T_g values ranging from 190 °C to 228 °C. For both phenylated and diphenylated series, T_g values increased with an increase of the sulfone linkage contents. This could be attributed to enhanced rigidity and polarity of the sulfone linkages. As expected, at the same level of sulfone linkages, DiPh-PES polymers always with more rigid and bulkier pendant groups had higher T_g values than those of corresponding Ph-PES analogues. In general, sulfonated polymers have higher T_g values than their non-sulfonated analogues, because the polarity of the sulfonic acid groups may enhance molecular chain interaction. The T_g values of Ph-SPES and DiPh-SPES were as high as 263–285 °C. For each of two series, the sulfonated polymers with higher $-SO_3H$ content showed higher T_g values.

As shown by the TGA curves, all the phenylated starting polymers possessed excellent thermal stability due to their fully aromatic structure. No weight loss below 400 °C was observed and the 5% weigh loss temperatures in air were above 505 °C. After sulfonation, the thermal decomposition temperatures decreased to a range of 334–354 °C, because of the lower decomposition temperature associated with sulfonic acid groups. It is very interesting to note that the DiPh-SPES series had better thermal stability than the Ph-SPES series. An obvious difference of 14–17 °C between DiPh-SPES and Ph-SPES copolymers is observed in Fig. 4 and Table 1. To our knowledge, this may be the first direct evidence that pendant-phenyl-sulfonated polymers have better thermal stability than the

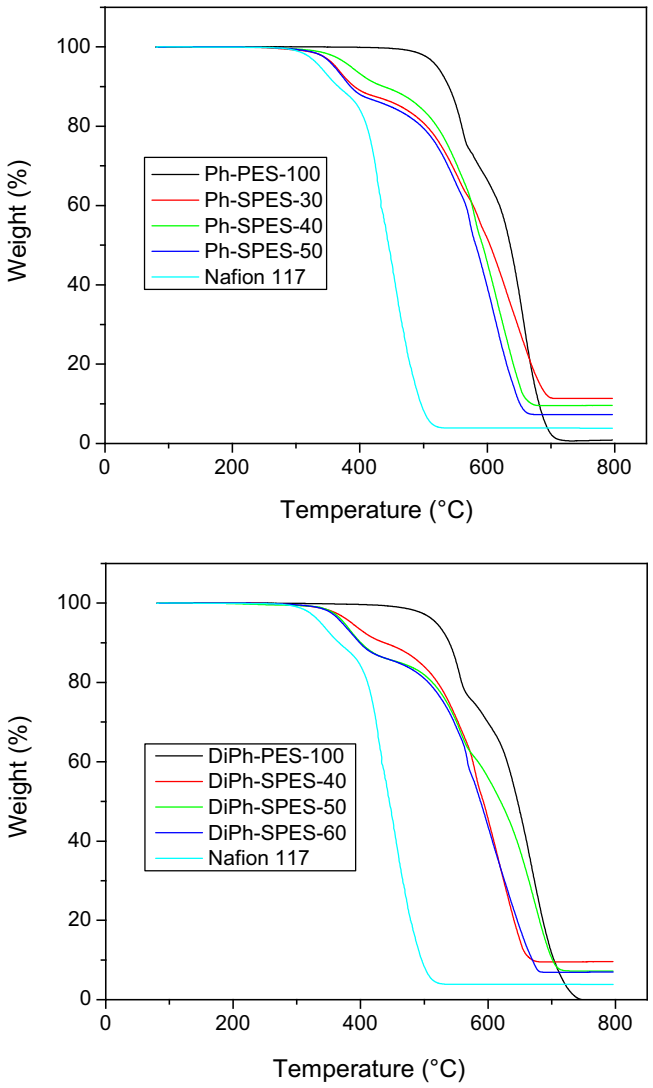


Fig. 4. TGA curves of the polymers in air.

Table 1
Viscosity and thermal properties of the polymers.

Polymer	η (dL/g)[a]		T_g (°C)[b]		TD (°C)[c]	
	non-S	S	*non*-S	S	*non*-S	S
Ph-PES-100	–	–	190	–	529	–
Ph-PES-60	0.52	1.6	209	284	516	336
Ph-PES-50	0.50	1.5	211	280	516	334
Ph-PES-40	0.49	1.5	220	278	517	344
Ph-PES-30	0.61	1.8	225	263	515	340
DiPh-PES-100	–	–	217	–	524	–
DiPh-PES-60	0.45	1.4	219	285	522	351
DiPh-PES-50	0.51	1.6	225	280	521	351
DiPh-PES-40	0.48	1.4	228	269	526	354

[a] Inherent viscosity of non-sulfonated and sulfonated polymers.
[b] Glass transition temperature. S refers to the sulfonated polymer, and non-S referred to the corresponding starting material.
[c] Onset temperature of decomposition.

Table 2
Mechanical properties of the sulfonated polymers in the wet state.

Membrane	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)	Oxidative stability (h)
Ph-SPES-50	24.5	0.37	54	0.6
Ph-SPES-40	39.8	0.72	116	2.5
Ph-SPES-30	38.9	0.54	52	>5.0
DiPh-SPES-60	21.6	0.36	139	1.2
DiPh-SPES-50	35.6	0.40	83	4.5
DiPh-SPES-40	40.9	1.00	60	>5.0
Nafion 117	24.5	0.16	316	>5.0

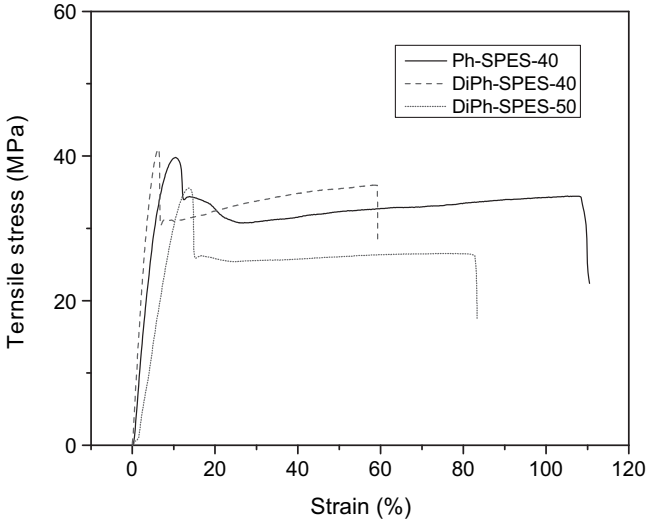


Fig. 5. Stress vs. strain curves of the membranes in the wet state.

corresponding main-chain-sulfonated (or a mixture of main-chain-sulfonated/pendant-phenyl-sulfonated) analogues. It was also observed these sulfonated polymers showed improved thermal stability over Nafion for the sulfonic acid degradation under the same testing conditions.

One of the key requirements for PEMs is good oxidative-hydrolytic stability under fuel cell operating conditions [3]. Oxidative attack by HO• and HOO• radicals mainly occurs in the hydrophilic domains, resulting in degradation of the polymer chains. Pendant-phenyl-sulfonated polymers, wherein sulfonic acid groups are attached to pendant groups distant from the polymer chain, are expected to have improved oxidative resistance over main-chain-sulfonated ones. The results evaluated in Fenton's reagent at 80 °C are shown in Table 2. It is generally the case that polymers having lower DS always exhibit better oxidative stability by this test [21]. It was interesting to note that the diphenylated series exhibited improved oxidative resistance over the mono-phenylated series, when compared at similar DS. For example, DiPh-SPES-50 (IEC ~ 1.70 meq/g) maintained film integrity after a 3 h treatment in Fenton's reagent, whereas Ph-SPES-40 (IEC ~ 1.60 meq/g) had already dissolved into Fenton's reagent after 2.5 h treatment. Especially, DiPh-SPES-40 (IEC ~ 1.50 meq/g) maintained film integrity after 4 h treatment, which suggests excellent oxidative resistance.

Good mechanical properties are another important factor for PEM applications. The tensile properties of the present copolymer membranes and Nafion 117 were tested in the wet state and are listed in Table 2. In comparison with Nafion 117, most of present aromatic PEM membranes possessed higher tensile strength in the range of 21.6–40.9 MPa and Young's moduli of 0.36–1.00 GPa. It was obvious that humidified Ph-SPES-60 and DiPh-SPES-60 membranes having high $-SO_3H$ content exhibited lowest tensile strength and moduli. Elongations at break were up to 52–139%, which suggested they were flexible materials. Several typical tensile curves are shown in Fig. 5, and the tensile strength results showed they were strong membrane materials. By comparison, the unsulfonated polymers had tensile stress in the range of 70–98 MPa and Young's moduli of 1.8–2.2 GPa, with elongations at break of 16–35%.

Water absorption, which is highly related to proton conductivity and dimensional stability of the membranes, is one of the typical characteristics of sulfonated polymers. To maintain high proton conductivity, a sufficient amount of water associated within the membrane is indispensable. However, the lower acidity of aromatic sulfonic acid compared with the fluoroalkyl sulfonic acid groups in Nafion leads to a higher DS requirement in order to obtain highly conductive hydrocarbon-based PEM materials. Depending on polymer design, an unfavorable trade-off effect of high DS or sulfonic acid content may be excessive water uptake, leading to unacceptable dimensional change or loss of dimensional integrity [3,10]. The preparation of highly proton conductive alternative hydrocarbon-based PEMs with high DS or sulfonic acid content, but having small dimensional change is one of the important topics of research for this class of materials. The water absorption and dimensional change in water at 30 °C and 80 °C were measured, and the results are listed in Table 3. For each of the series, both water uptake and swelling ratio increased with an increase of sulfonic acid ionic contents at given temperature. At room temperature, all the membranes exhibited very good water absorption and swelling ratio (swelling ratio $\leq$20%) characteristics. At 80 °C, Ph-SPES-50 and DiPh-SPES-60 membranes, both having high IEC values, did not retain dimensional shape. However, DiPh-SPES-50, DiPh-SPES-40 and Ph-SPES-30 exhibited acceptable dimensional change (swelling ratio $\leq$30%), even at elevated temperature.

The proton conductivities of the membranes were estimated from AC impedance spectroscopy data and the results at different temperatures are presented in Fig. 6. Generally, the conductivities of all the samples increase with temperature in the range of evaluated temperatures. Besides this, for both DiPh-SPES and Ph-SPES series, the membrane with higher IEC value had higher proton conductivity. All the membranes possessed room temperature conductivities higher than 0.01 S/cm, which is conventionally regarded as a minimum value requirement for practical PEM application in FC. DiPh-SPES-60 exhibited higher proton conductivities than that of Nafion 117 throughout the temperature range of 30 °C–70 °C,

Table 3
Water uptake and proton conductivity of the membranes.

Polymer	IEC (meq/g)[a]		WU (%)[b]		SR (%)[c]		σ (S/cm)[d]		MP (cm^2/s)[e]
	Calc.	Exp.	30 °C	80 °C	30 °C	80 °C	30 °C	80 °C	30 °C
Ph-PES-50 (~82 μm)	1.95	1.72	50.6	–	19.2	–	59	0.141	5.1×10^{-7}
Ph-PES-40 (~86 μm)	1.59	1.52	32.8	400	10.6	55	29	0.086	2.8×10^{-7}
Ph-PES-30 (~92 μm)	1.21	1.13	12.5	22.0	3.8	4.6	10	0.036	9.4×10^{-8}
DiPh-PES-60 (~83 μm)	2.11	1.91	55.4	–	20.0	–	83	0.147	7.0×10^{-7}
DiPh-PES-50 (~87 μm)	1.81	1.63	41.5	85.0	13.8	30.0	46	0.098	4.6×10^{-7}
DiPh-PES-40 (~95 μm)	1.50	1.35	14.8	26.6	8.7	11.5	18	0.057	1.4×10^{-7}
Nafion 117 (~180 μm)	0.90	0.90	22	30	14	20	57	0.112	1.5×10^{-6}

[a] Ion exchange capability.
[b] Water uptake.
[c] Swelling ratio in plane direction.
[d] Proton conductivity.
[e] Methanol permeability.

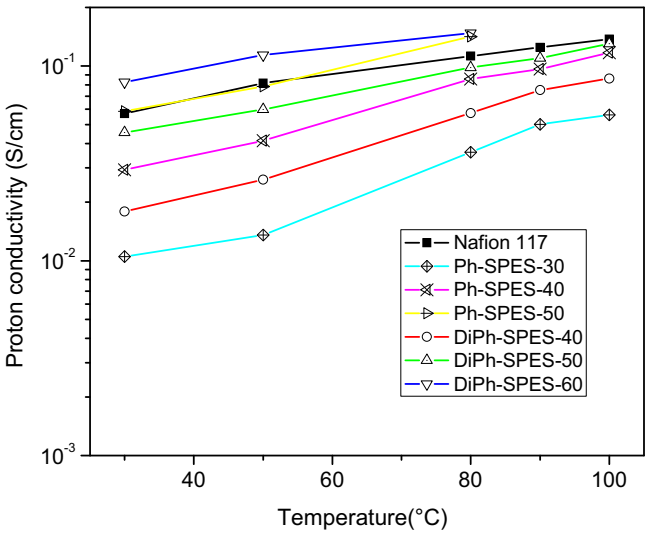


Fig. 6. Proton conductivities of the membranes and Nafion 117.

although it did not retain dimensional shape at elevated temperature. At 100 °C, proton conductivities of DiPh-SPES-50 and Ph-SPES-40 were as high as 0.130 and 0.117 S/cm, respectively, which are comparable to the value of 0.138 S/cm for Nafion 117.After making comparisons between water absorption, proton conductivity and methanol permeability, it was shown that the membranes having higher water uptake always showed higher proton conductivity and lower methanol permeability. Certainly, this is highly relevant with the content of ionic groups.

One significant drawback for Nafion in DMFC application is its high methanol crossover. This limitation is associated with the microstructure of Nafion, whereby interconnected ionic domains strongly contribute to its high proton conductivity, but at the same time contribute to fast methanol diffusion [25]. As shown in Table 3, the methanol permeability values of the membranes were in the range of 7.0×10^{-7}–9.4×10^{-8} cm^2/s at 30 °C, which is several times lower than the value of Nafion 117 of 1.55×10^{-6} cm^2/s. The membranes having a combination of high proton conductivity and low methanol crossover are being pursued for DMFC system. It is facile to evaluate the membranes through drawing a performance trade-off plot containing both methanol permeability and proton conductivity [26]. As shown in Fig. 7, all the data is situated at the right top corner of the plot.

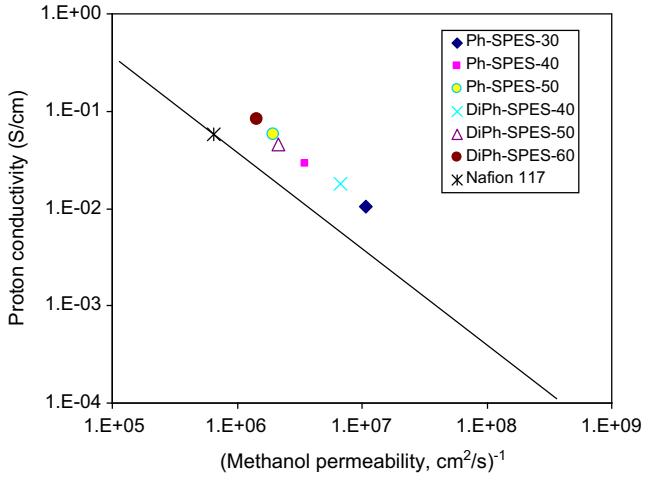


Fig. 7. Methanol permeability vs. proton conductivities of the membranes and Nafion 117.

Combined with all the other physical properties, DiPh-SPES-50 appears to be the most promising material of the present series for DMFC application.

4. Conclusion

A bisphenol monomer, 2,5-diphenylhydroquinone, was synthesized via a one-step route. Derived from phenylhydroquinone and 2,5-diphenylhydroquinone, two series of starting materials, mono-phenylated poly(ether sulfone)s (Ph-PES) and diphenylated poly(ether sulfone)s (DiPh-PES), were synthesized via a typical nucleophilic substitution polycondensation. These polymers were sulfonated for extended reaction times, to observe the maximum DS achievable, and the site of sulfonation. Under the same mild sulfonation conditions using commercial concentrated sulfuric acid at room temperature, Ph-PES polymers and DiPh-PES polymers exhibited different behavior. NMR analysis revealed that fully sulfonated di-phenylated-acid SPES polymers could be prepared based on 2,5-diphenylated polymers. It was noted that the SPES containing di(4-sulfonic acid)phenyl pendants (DiPh-SPES) exhibited extremely good thermo-oxidative stability. For example, from TGA results, an obvious difference of 14–17 °C between DiPh-SPES and Ph-SPES copolymers was observed. Meanwhile, both DiPh-SPES and Ph-SPES showed improved thermal stability over Nafion under the same testing conditions. The sulfophenylated polymer was also shown to have better oxidative stability than the one containing main-chain sulfonation, as shown by the Fenton test. In comparison with Nafion 117, these membranes possessed low methanol permeability in the range of 7.0×10^{-7} to 9.4×10^{-8} cm^2/s at 30 °C. DiPh-SPES-50 and Ph-SPES-40, with IEC values of 1.63 and 1.52 meq/g respectively, also exhibited high proton conductivity of about 130 mS/cm and 117 mS/cm at 100 °C, which are comparable values to Nafion 117.

Combined with its good mechanical properties and low dimensional change in hot water, a diphenylated polymer, DiPh-SPES-50, is a promising PEM material for PEMFC and DMFC applications.

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